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The investigation of the deleterious action of certain metals on the cyanide process for gold

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THE INVESTIGATION OF THE DELETERIOUS ACTION OF CERTAIN METALS ON THE "CYANIDE PROCESS" FOR GOLD.

It is our desire in this thesis to try and verify, if possible, the results or conslusions published by several authorities on cyaniding regarding the deleterious action of certain metals on potassium cyanide, and also, to make experiments on several very refractory ores for the purpose of devising some economical method of treatment.

The first ore under consideration is one that was brought here by John Rice for the purpose of determining whether it was applicable to the cyanide treatment.

The ore, as originally treated at the mine, was by the straight free milling process of stamping, and amalgamating the gold on plates. Owing to some peculiarities, the ore upon crushing produced a great amount of slimes, which was of a clayey character, and would continually clog the screens. (Probably due to al which was found present.)

The ore is a silicious iron ore with the iron in the form of oxide (hematite).

A qualitative analysis showed the following metals:

Si, Fe, Ca, Al, Cr, Au, and Ag, and Cu.

Quantitative analysis gave:

SiO_2 = 25%

Fe_2 = 40%

Cu = 1%

TREATMENT OF COPPER ORES.

So far, with the exception of the "Hunt Process," roasting appears to be the only practicable method of rendering these ores available for cyanide treatment, and even then the cost is usually so high as to call for the employment of concentrating and pyritic smelting.

Several attempts have been made to remove the copper, when it exists in a soluble condition, by leaching with a solution, 5% H_2SO_4. Very poor results were usually obtained, but by boiling with a dilute solution of H_2SO_4 gave very high extraction.

Roasting has also been used with very good results, but the consumption of K C N was usually high.

The following experiments will be carried out on an ore especially selected as representing the class of cuperiferous ores containing much acid, and copper in the form easily soluble in cyanide, thus causing abnormal consumption.

The first series of test were made for the purpose of ascertaining,

1st; the amount of KCN consumed by RAW ore, then

2nd; treating with caustic soda wash to destroy acid.

3rd; wash out soluble salts and test for KCN consumed.

4th; by treating ore with H_2SO_4 to dissolve the Cu.

The ore was very carefully sampled and then crushed to the following sizes:

20#, 40#, 60#, 80#, and 100#.

The following tests were made for determining:-

1st: The proper strength of solution to be used which would extract the highest percentage of gold with the smallest consumption of itself.

2nd: The shortest time that the ore can be left in contact with it, still giving high extraction.

3rd: How coarse can the ore be kept while yet allowing a successful extraction.

The apparatus consisted of a number of half gallon jars, with screw and clamp tops. The amount of ore used in each was 150 grams, and 300 c.c. of H_2O, including KCN solution.

Strength of KCN solution was 4.11%.

EXPERIMENTAL TEST TO DETERMINE THE BEST STRENGTH OF SOLUTION.

Strength of Sol. 4.11% Assay 1.48 oz.

No.	% KCY	Time Hours.	No c c of stock sol.	No c c of H_2O	Assay of Tailings.	Extraction %	Mesh.
1	.1	48	7.3 c c	292.7 c c	1.24	1.62	40
2	.15	48	10.95 c c	289.1 c c	1.215	1.79	40
3	.2	48	14.6 c c	285.4 c c	1.155	2.19	40
4	.3	48	21.9 c c	278.1 c c	1.18	2.02	40
5	.5	48	36.5 c c	263.5 c c	1.15	2.23	40

It is very evident from the above table that the gold is not in a condition to be acted upon by the cyanide, or either there is some powerful agent present that consumes the cyanide; probably sulphuric acid.

The next set of tests made at the same time as the above, but producing no better results, are as follows:

(This series was to determine the time.)

Experimental Test No. 2.

No.	% KCN	Time Hours	Mesh	c c of stock sol.	c c of H_2O	Assay of Tailings	Extraction %
1	.3	24	40	21.9	278.1	1.34	.94
2	.3	48	40	21.9	278.1	1.21	1.82
3	.3	48	40	21.9	278.1	1.17	2.09
4	.3	72	40	21.9	278.1	1.18	2.02
5	.3	72	40	21.9	278.1	1.16	2.16

In this series of experiments it was found by testing the solutions after leaching that the cyanide in every case was wholly or nearly all consumed.

The next set of tests were made for the purpose of trying to eliminate those agents which were consuming so much cyanide.

This preliminary treatment consisted of roasting No 1 and No. 2, alkaline wash No. 4, and H_2SO_4 treatment of No. 3.

Experiment Test No. 3.

No. Test.	Preliminary Treatment.	% KCN	Mesh	Assay of Tailings	Extraction %	%KCN after Treatment.
1	Roast	.3	80#	.41 oz	71.7	.025
2	"	.3	40#	.24 "	83.57	.19
3	H_2SO_4	.3	80#	1.14 "	23	.13
4	KOH	.3	40#	1.11 "	25	.015

From the above data it is obvious that roasting is absolutely necessary in order to give anything like a satisfactory extraction with the cyanide.

On the samples tested with H_2SO_4 and the KOH wash, previous to cyanide treatment, the results were about the same, and very unsatisfactory, it being almost impossible to filter the slimes.

Although with the H_2SO_4 treatment the consumption of cyanide was much less than with the KOH treatment, which was probably due to the H_2SO_4 taking up some of the iron salts and these being removed by washing previous to cyanide treatment.

It will also be noticed in the case of the two roasted ores that in the first the whole or nearly all the KCN was consumed, while with the second only .11 was taken up. This was probably due to the fact that in the first case the ore was roasted over a gas lamp, and in the second it was roasted in furnace to high heat. In the first case the heat was probably high enough to place the gold in a condition applicable to cyanide, but not sufficient to render or destroy the deleterious action on cyanide.

Following the conclusions drawn from the above data, a new series of tests was made on roasted ore in which the strength of solution, and the time will be varied.

We will also make four tests on the raw ore to prove conclusively to our own satisfaction that the direct treatment on the raw ore is impossible, as far as a good extraction is concerned.

Treatment of Roasted Ore.

	Weight.	Assay.
Raw Ore	200 grams	1.48 oz
Roasted Ore	166.6 "	1.60 "

Loss of weight in roasting = 16.66%
" " gold from roasting, based on one ton:

		Gold in A T	Total Au
Raw 2000#	= 29166 A T	.00148	43.16568
Roast 1333#	= 26696 A T	.00160	42.71360
			.45208

$\frac{4520}{43.165}$ = 1.04% loss in roasting.

Experimental Test No. 4.

Treatment of Roasted Ore.

No.	% KCN	Mesh	Time	Strength of Sol at end of treatment	Assay of Tailings, 1/2 A T	Extraction based on raw
1	.1	40	48	.07	.09	87.76%
2	.2	40	48	.17	.07	89.59%
3	.3	40	48	.24	.077	89.35%
4	.3	40	24	.21	.175	77.66
5	.3	40	72	.23	.067	90.31
6	.2	40	72	.16	.06	90.84

By roasting the ore, and judging from the results obtained, its applicability to the cyanide treatment is assured.

In the above tests instead of adding pure water to my storage solution to bring it to the required strength, a dilute NaOH solution was added.

There seems to be no objection to using the alkali solution, as above cited, so far as the dissolving power of the cyanide is concerned, but authorities claim that by too much alkali are caused complications in the extraction or precipitation boxes. This is probably due to the fact that when causte soda is used as a neutralizing agent it has a tendency to foul the solution, and cause the formation of ferrocyanide of zinc in the precipitation boxes.

In some works it was found that when a very small amount was used, that towards the end of the leaching operation when the outgoing solutions were diluted with wash water, the liquor

become so fouled with slimes as to be practically worthless. This is explained,(according to Bosqui) that the prescence of certain salts facilitates filtration by retaining in place the finely divided particles which would otherwise clog the filter and foul the filtrate.

This has been obviated to some extent by the addition of pulverized lime with the ore. This seems to have no deleterious action on the cyanide solution, although an excess is said to increase the consumption of cyanide in the precipitation boxes.

It was also found in my experiments in treating the raw ore with a NaOH solution, that the increase of slimes was quite noticeable, although with this ore it was found that the slimes produced with pure water treatment were so great that the direct treatment would have been impossible, even though the raw ore was applicable to cyanide.

As to the required amount of alkali agents to be used, Mr. James, the South African authority, states that the best empirical course to follow is to maintain the alkalinity - by the addition of lime or soda - of the strong solution to just such a point that, "on the addition of soda to a sample, the cyanide test does not rise."

He also claims that when just sufficient alkalinity is obtained, it benefits the dissolving power of the double cyanide of zinc and potassium, plus alkali, with the subsequent diminution of the amount of free cyanide to be added to the charge to restore it to its required strength.

It was my intention on these last tests to vary the mesh more than I did, but owing to the fact that our supply of ore was limited, I had to use that which I had most of.

Now, calculating from the above data that a .2% on forty mesh and 72 hour contact, gave the best results, it will also be noticed that a .3 with same mesh and 24 hours gave a much lower extraction, which I think is sufficient proof that 24 hours is too short a time without agitation. I will also note that these samples were shaken up only four times during the treatment.

In both cases a .2% gave a higher extraction than a .3% on both the 48 and 72 hour contact.

TESTS ON RAW ORE.

No. Test.	% KCN	Mesh	Time	Strength of Sol. at 24 hrs	At 72 hrs.	Assay of Tailings	Axtraction
1	.3	80	72	.02	.12	1.10 oz	25.7%
2	.5	80	72	.05	.28	1.12 "	24.6%
3	.3	100	72	Trace		1.09	25.7
4	.5	200	72	.02	.26	Lost	

It is quite evident from the above tests that the cyanide treatment on the raw ore would not be a paying proposition. The consumption of cyanide being very high and the extraction very low.

The slimes produced in this test were so great that it required nearly two hours to filter two assay tons. On this fact alone would preclude the possibility of the raw treatment on an economical scale. It perhaps could be done, but would require a large number of vats and a devise for the removal of the slimes before percolation.

I will not attempt to design a plant for the treatment of this ore, but I will outline or devise a scheme for the treatment preparatory to its entering the vats for treatment.

In some cases of American practice on roasted ore, it has been the custom to roast before crushing, but it seems to me that crushing before roasting would be the wiser plan.

Scheme For Preparing Ore For Treatment.

1. Pass through large Gates crusher.
2. Pass through small Gates crusher.
3. Crushing rolls to 4 mesh.
4. Conveyor to storage bins.
5. Tubular dryer (heated to 300 degress F.)
6. Elevators.
7. Coarse screens.
8. 36" rolls crushing to 8 mesh.
9. Screens.
10. 15" X 26" rolls crushing to 30 mesh.
11. Crushed ore bin.
12. Roasters.
13. Conveyors.
14. Coolers.
15. Conveyor for cooled ore to vats.

The next ore upon which tests were made is an iron sulphide, containing Si, Al, Ca, Fe, Cu, S, Au and Ag.

Analysis of Ore:

SiO_2	=	18.22 %
Fe	=	28.21 "
S	=	34.31 "
Cu	=	1.14 "
Al_2O_3	=	5.14 "
$CaCo_3$	=	8.21 "
Au	=	3.30 "

The same tests were made on this ore as on the other one, with the addition of what is known as the "Hunt Process for Treating Auriferous Copper Ores by the Cyanide Method."

Experimental Test No. 1.

Treatment of Raw Ore.

Stock Sol 4.368% Assay 3.30 oz.

No. of Test.	% KCN	Time Hrs.	No. c c of Stock Sol.	No. c c of H_2O	Assay Tailings	Extraction %
1	.1	24	6.8	293.2	2.82	14.54
2	.2	48	13.6	286.4	2.60	21.21
3	.5	48	34.0	266.0	1.70	48.48
4	.3	48	20.6	279.4	2.46	22.12
5	.2	48	13.6	286.4	1.94	41.21
6	.2	72	13.6	286.4	1.88	43.03

The above tests were made on a raw ore to see if a fair extraction could be obtained, and from the results found it is plainly seen that the ore must be treated in some other way.

The tests made on the solutions after treatment showed that the KCN had all been used up, showing that some agent eats up the KCN before it can act on the Au, which is probably due to some copper salt.

No. 4 was treated cold with H_2SO_4, and this seemed to cause less extraction.

No. 5 was treated hot with H_2SO_4 which gave a little better extraction, as most of the Cu was dissolved out.

No. 6 was washed with NaOH.

When H_2SO_4 was used it made a great amount of slimes, which made it difficult to filter, requiring more time and labor.

No. 3 gave the best extraction, showing that the greater strength of cyanide gives the best extraction, but it is entirely too low to make the raw ore an economical way of treatment.

Experimental Test No. 2.

Treatment of the Roasted Ore. Assay 3.84 oz.

No. of Test	% KCN	Time Hrs	No c c stock sol.	No. c c H_2O	Assay Tailings	Extraction %
1	.1	72	6.8	293.2	.31	89.19
2	.5	48	34.0	266.0	.328	88.44
3	.3	48	13.6	286.4	.66	76.75
4	.2	72	13.6	286.4	.28	90.12
5	.3	24	20.6	279.4	.315	88.91
6	.5	72	34.0	266.0	.27	90.51
7	.3	48	20.6	279.4	.296	89.57

Raw ore 200 grams.

Roasted Ore 167.4 grams.

Loss in weight 16.3%

Time of roast, 4-1/2 hours.

	Weight	Assay	Weight of Au in grams.	% lost in Roast
Raw Ore	200	Au 3.30 oz	.0226	$\frac{.0006}{.0226}$ = 2.65%
Roasted Ore	167.4	3.84 "	.0220	

In the above test a very good extraction is obtained; the best being .5% KCN and 72 hours time, while .2% KCN gives almost as good an extraction. From the results obtained, time of contact with the KCN solution seems to be the main factor, although a very good extraction is obtained in No. 7, the time being 48 hours.

In No. 7 the roasted ore was washed with NaOH solution first, which gave a better extraction than No. 3, showing that the ore must be of an acid character, probably due to the presence of $FeSO_4$.

In roasting FeS_2 we obtain the following reaction:

$$2\ FeS_2 + 11O = Fe_2O_3 + 4\ SO_2$$

Some sulphates are also formed as:

$$3\ FeS + 11\ O = 2\ SO_2 + Fe_2O_3 + FeSO_4$$

The $FeSO_4$ reacts on KCN, as follows:

$$2\ KCN + FeSO_4 = K_2SO_4 + FeCu_2$$ (ferrous cyanide being formed) or

$$6\ KCN + FeSO_4 = K_2SO_4 + K_4FeCu_6$$

The solutions were all tested after treatment, and only a trace of KCN could be found in Nos. 2 and 6.

From the above results, we conclude that the ore must be roasted before treatment by the "Cyanide Process," and that then a very good extraction can be obtained.

HUNT'S PROCESS FOR THE TREATMENT OF AURIFEROUS COPPER ORES BY THE "CYANIDE METHOD."

Owing to the known solubility of many copper salts in sulphuric acid, it would seems that to treat the ore with sulphuric acid would be the best method. But the consumption of acid is high, when lime or magnesium carbonates are present in the ore, as they often are in highly silicious ores.

Moreover, when acid is used the ore has a tendency to pack, and it causes a large amount of slimes. A neutralizing agent, such as a solution of sodium hydroxid, must follow the acid treatment, or more cyanide will be decomposed than if the ore had been treated direct, which is shown by the following reaction:

$$2\ KCN + H_2SO_4 = K_2SO_4 + 2\ HCn$$

This is an additional expense, as additional solutions and thorough washings are necessary, and if water is not plentiful it would be very expensive.

This treatment has essentially three stages:

(1) Leaching the ore with dilute H_2SO_4

(2) Neutralizing with NaOH.

(3) Cyanide treatment proper.

The time of first depends not only on the amount of copper in the ore, but the character of the bases with which the sulphuric acid will combine.

The percolation rate of the pulp plays an important part; it may be slower with sulphuric acid than with other liquors, as there is a tendency with sulphuric acid to form gelatinous silica having cementing properties.

Hunt's Process has been used in California with great success. It consists in leaching auriferous copper ores with an ammonical cyanide solution.

It has also been found very efficient on tailings, which have been previously treated by pan-amalgamation, in which copper sulphate has been used, and formerly could not be treated by the "Cyanide Process."

Hunt's Method is a one stage process. It depends upon the protective influence of ammonia, as well as its dissolving power for copper. The ammonia and cyanide are employed in the same solution.

In treating cuperiferous gold ores by this process the strength of the solution in ammonia is varied according to the copper contents of the material to be treated.

Any salts of ammonia may be used instead of ammonium hydroxide, provided lime or some alkali is added to the ore. An ore containing 1% copper requires 7 to 8 lbs of ammonium chloride to the ton, and the strength of potassium cyanide solution need not be more than .15 to .2% with the addition of 7 to 8 lbs of buried lime per ton of ore, it has brought the loss down to 1 lb of potassium cyanide per ton of ore, and a very high extraction was obtained.

Experimental Test No. 3.

TREATMENT OF THE RAW ORE BY "HUNT'S PROCESS."

No. Test.	KCN %	Time Hours	No. c c stock solution.	No. c c NH_4OH	Assay Tailings	% KCN end of treatment	Ext. %
1	.5	24	34.0	266.0	2.64	.194	20.00
2	.2	48	13.6	286.4	2.20		33.33
3	.3	48	20.6	279.4	2.42	.065	26.66
4	.1	72	6.8	293.2	3.10		6.06
5	.2	72	13.6	286.4	1.96		42.42
6	.3	72	20.6	279.4	1.88	.045	43.03
7	.5	72	34.0	266.0	1.80	.18	45.45
8	.5	48	34.0	266	2.32	.21	32.96

The above series of tests were made on the raw ore, and the extraction was not any better than the tests previously made by the ordinary method; the only difference being a saving in potassium cyanide, as shown by the strength of the solutions after treatment.

Experimental Test No. 4.

TREATMENT OF THE ROASTED ORE BY "HUNT'S PROCESS."

No of Test	% KCN	Time Hours	No. c c stock solution.	No. c c NH_4CH	Assay Tailings	% KCN after treatment	Ext. % based o roasted ore
1	.1	24	6.8	293.2	.44		89.54
2	.2	24	13.6	286.4	.31		89.19
3	.1	48	6.8	293.2	.342		88.18
4	.2	48	13.6	286.4	.174		93.88
5	.3	48	20.6	279.4	.16	.09	94.36
6	.5	48	34.0	266.0	.21	.32	92.60
7	.1	72	6.8	293.2	.32		88.87

Experimental Test No. 4. (Continued.)

No. of Test.	% KCN	Time Hours	No. cc stock solution	No. cc NH_4OH	Assay Tailings	% KCN after treatment	Ext. % based on roasted ore
8	.2	72	13.6	286.4	.166		94.15
9	.3	72	20.6	279.4	.28	.04	90.12
10	.5	72	34.0	266.0	.18	.28	93.66

In the above series of experiments very good extractions were obtained. In six cases the extraction was greater than without the use of NH_4OH, and a great saving in KCN was obtained.

The ore filteres good after treatment, but not as fast as without the use of NH_4OH, but much better than when H_2SO_4 was used.

The 72 hour solutions were the longest in filtering, but in all cases much quicker then in the"H_2SO_4 method."

The increased extraction is probably due to the energetic oxidizing powers of a solution of cupric oxide dissolved in ammonia. When an excess of cupric oxide is dissolved in ammonia containing less cyanide than will combine with the copper, then cupric cyanide of the alkali is formed, which exerts a solvent action on gold equal to that of cyanide of potassium itself.

When cupric oxide acts on potassium cyanide alone $CuCu_2$ is formed, which becomes $CuCu_2$, 2KCN if an excess, showing that the loss in KCN is great.

The solution containing NH_4OH and KCN cannot be tested in the ordinary way for KCN, as the $AgNO_3$ method is not applicable for solutions containing ammonia, and must be treated as follows:

To the solution add an excess of mercuric chloride or oxide, with a few drops of caustic soda. Boil off the ammonia, causing precipitation of the base metals. Filter and wash. Precipitate the mercury in the filtrate with a slight excess of sodium sulphide, neutralize excess of the alkaline subphide with carbonate or boric acetate of lead. Filter and wash, and filtrate with silver nitrate solution in the ordinary way.

In all cases 100 grams of ore was taken and the ore was ground to 80 mesh. Conc. NH_4OH, diluted 50%, was used in Hunt's method.

COMPARISON OF TWO METHODS.

Experiment No. 1.

Test.	Ore.	% KCN.	Time Hrs	% KCN Consumed.	Lbs KCN used per ton of ore.	Lbs KCN saved per ton of ore	Best Ext. %
3	Raw	.5	48	100	30	———	48.4
6	"	.2	72	100	12	———	43.0
5	"	.2	48	100	12	———	41.2

Experiment No. 3 (Hunt's)

Test.	Ore.	% KCN	Time Hrs	% KCN consumed.	Lbs KCN used per ton of ore	Lbs KCN saved per ton of ore	Best Ext. %
7	Raw	.5	72	64	30	10.8	45.45
6	"	.3	72	85	18	2.7	43.02

Experiment No. 2.

Test	Ore	Time Hrs	% KCN	% KCN Consumed	Lbs KCN per ton	Lbs KCN used ore saved per ton of ore	Best Ext. %
6	Roasted	72	.5	100	30	———	90.51
4	"	72	.2	100	12	———	90.12
7	"	48	.3	100	18	———	89.57

Experiment No. 4. (Hunt's)

Test.	Ore	%KCN	Time Hrs	% KCN Consumed	Lbs KCN used per ton of ore	Lbs KCN saved per ton of ore	Best Ext. %
5	Roasted	.3	48	70	18	5.5	94.36
8	"	.2	72	100	12		94.15
4	"	.2	48	100	12		93.88
10	"	.5	72	44	30	16.8	93.66
6	"	.5	48	36	30	19.2	92.60
9	"	.3	72	86.6	18	2.4	90.12
2	"	.2	24	100	12	89.19	

The results on the raw ore are very unsatisfactory in both methods, but there is a saving of cyanide by "Hunt's Method."

The results on the roasted ore give a very good extraction by either method, but Hunt's Process gives a surprisingly high extraction, being 94.36% with a .30% KCN solution, with a saving of .09% KCN.

The best extraction by the common method is 90.51% with a .5% KCN solution, although the .2% KCN solution gives almost as much. The difference between the best extractions of the two processes is 3.85%, which would amount to .117 ozs more gold valued at $2.41 in the Hunt's, and using 17.5 lbs less of KCN to the ton, but it has the extra cost of NH_4Cl and CaO.

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Advantages of the Hunt's Process:

(1) Many ores can be treated that are low grade.

(2) Increased economy by reduction of the consumption of cyanide.

(3) It is simple, thus saving time and labor.

(4) The cost of the reagents are cheap compared to cyanide. Part of this may be made up by the value of the copper extracted.

(5) Unlike the acid treatment, calcareous ores are desired.

(6) There are no limitations to the copper contents of of the ores, but for extremely high grade copper ores we would have to recover the ammonia.

The scheme given for ore No. 1 would apply to this ore also.